CONTRACT REPORT NUMBER 59215-01-ST

CONTRACTOR: University of Sherbrooke

REQUISITION NUMBER 23440-5-9215

Project title: **"The hydrocracking of individual components isolated from heavy oils"**

Reference: Contract D.S.S. Cont. File No. 23440-5-9215/01-ST
Serial No. 37ST.23440-5-9215

Prepared for: Energy, Mines & Ressources Canada/Canmet/Energy Research Labs

Prepared by: E. Chornet, P.K. Tiwari, M. Heitz and W.H. Dawson

The objective of this work was to develop a better understanding of which chemical fractions (i.e. families) present in heavy oils are responsible for processing difficulties (i.e. coke formation), which convert to beneficial (i.e. light) products and how this interplay can be controlled by the processing conditions.

To accomplish the above objective the project was structured as follows:

- development of a reproducible separation methodology to fractionate the heavy oils into constitutive chemical families
- experimental investigation, under characteristic hydrocracking conditions, of the conversion of the individual constitutive families
- provide detailed material balances
- develop a mechanistic understanding of the interplay between H-transfer and recondensation reactions during hydrocracking.

The project was organized in tasks to facilitate control of objectives through analysis/synthesis of results.

The first task was concerned with the development of hydrocracking procedures. Two autoclaves were used: a 500 ml system equipped with a magnetic stirrer and a microautoclave having a capacity of 12 ml. The microautoclave was developed to study the small quantities (~ 5-8 g) derived from the chromatographic separation procedure. Agitation of the microautoclave was conducted by bubbling hydrogen using a fine grid as dispersor. A reflux condenser was also installed to maintain the light hydrocracked materials in contact with the reactants at all times. In both autoclave systems heating of reactor contents was made through immersion in a eutectic salt bath. Uniform temperature profiles were thus obtained aided by the agitation in both autoclave systems. The products of both autoclaves were analyzed for total gas composition (via G.C.) and the usual maltenes, asphaltenes and coke separations.

5pp

MICROMEDIA

An initial batch of screening experiments was conducted in the 500 ml autoclave to provide detailed material balances from which the hydrocracking operational conditions were selected. The range comprised between 420-460°C and 0-60 min as reaction time at reaction temperature, with total reactor pressure of 2000 psig was chosen as most characteristic of uncatalyzed hydrocracking for the Athabasca bitumen vacuum topped bottoms used as a prototype material. Coke formation could be maintained low (< 6% of initial heavy oil charged) at temperatures of 420°C and reached 30% at the highest severities while the pitch conversion (525°C) was maintained between 55 and 70%. The initial high asphaltene content of the heavy oil (34.6%) was significantly reduced with all treatments and a linear correlation between pitch conversion and asphaltenes conversion was derived.

In order to better understand how the hydrocracking affected both maltenes and asphaltenes as well as how the coke (i.e. toluene insoluble) was formed an elaborate, yet operationally simple, chromatographic separation system was developed. Thus the maltenes were separated by a silica/alumina column using, sequentially, three solvents of increasing polarity. The first fraction eluted with pentane and it was composed of saturates while a second fraction also eluted, but at a later time, with pentane provided mono-and di-aromatic molecules. The third fraction was eluted with pentane/CH_2Cl_2 and provided the polyaromatics whereas a four fraction eluted with CH_2Cl_2/MeOH gave the polar components of the maltenes. This procedure was progressively improved until material balances (the sum of the four eluted fractions) closed within 10%. When the chromatographic procedure developed for the maltenes was applied to the products resulting from the uncatalyzed hydrocracking it was demonstrated that the key features during hydrocracking are a marked decrease of the polar compounds (2/3 of the polars initially present in the untreated heavy oil are transformed at temperatures beyond 440°C and 1/3 rapidly convert to lighter products in the range 420-430°C). The polyaromatics also show an important decrease. About 1/2 of the initially present polyaromatics in the untreated heavy oil are converted to lighter products (i.e. gases, saturates and mono- and di-aromatics) as a consequence of hydrocracking at or beyond 445°C. Since the initial asphaltenes also decrease drastically during the uncatalyzed hydrocracking treatment and the coke formation increases markedly it was not clear at this point whether the coke increase is due entirely to the asphaltenes or whether the polyaromatics and polars from the maltenes also participate to the coke formation. It was expected that processing of the individual fractions will facilitate responses to this key question as it will be reported later.

In order to better understand the nature and the characteristics of the asphaltenes, we attempted to separate them using a silica packed column. The initial fractionation followed reported procedures and seven solvents of increasing polarity were used. The separation strategy was progressively changed to obtain four fractions: a toluene or toluene/15% hexane eluted fraction which contains essentially residual saturates and aromatics; a second fraction eluted with chloroform which contains non-basic polar compounds; a third fraction eluting with chloroform/3% ethanol which elutes preferentially heterocyclic basic compounds; and a fourth fraction eluted with chloroform/20% methanol which elutes the heavier asphaltenes having high functionalities. Material balances were better than 5% for this procedure.

The chromatographic procedures used allowed to define and optimize the sequence of solvents. They also provided the ratios maltenes/silica/alumina and asphaltenes/silica better suited for the separation as well as the required flow rates. The procedures were developed for 3 g of maltenes and 1 g of asphaltenes.

A further challenge of the project was to scale-up the separation procedure so that significant amounts of the four maltene and asphaltene fractions could be obtained for the hydrocracking studies of the individual fractions. We opted for a multicolumn separation system based on multiples of a prototype column having 10 cm as internal diameter and admitting up to 90 cm of packing. This system allows the fractionation of about 10 g of asphaltenes and 30 g of maltenes per column. Ten columns were built and eight of them can be operated in parallel to treat about 80 g of asphaltenes and 240 g of maltenes. Prior separation of asphaltenes and maltenes using toluene/pentane is required. The results obtained with the large scale preparation system were conclusive as to the reproducibility and feasibility of the overall operation. Care in the manipulation of the samples to avoid oxidation during prolonged storage as well as proper solvent removal via vacuum evaporation are required if clean fractions are to be obtained.

In summary, the chromatographic procedure provided a tool to monitor the characteristics of the products and, also, allowed us to begin to process the individual fractions derived at the preparative scale. Let us also mention that FTIR and ^{13}Cnmr have begun to be used to determine the chemical functionalities of the fractions and ascertain that the fractionation accomplishes the separation objective into families of compounds chemically uniform.

The total maltenes as well as a new batch of Athabasca bitumen vacuum topped bottoms were studied in the microautoclave system to understand their hydrocracking features. The vacuum bottoms behaved very similarly to the previous batch used in the screening experiments. Similar features were confirmed in terms of product distribution. It was also clear from these experiments that the inception of hydrocracking occurred at relatively low severity since at 400°C and 30 min as reaction time the asphaltenes decreased significantly (38.6% in the initial feedstock to 27.8% in the treated material) with a corresponding increase in maltene-saturates (3.4% to 10.5%) and maltene- mono/ and di/aromatics (3.2% to 6.8%) with very little formation of coke (0.8% to 1.8%) and minimum gas production (1.2%). It was also significant to observe that the maltenes-polyaromatics begin hydrocracking at 420°C and 30 min while the asphaltenes did not decompose (i.e. hydrocrack) further on going from 400°C to 420°C. The maltenes-polars are slightly hydrocracked at 400°C yet their decomposition is significant at 420°C and 30 min (from 15.5% in the initial feedstock to 13.7% at 400°C and 9.4% at 420°C). Coke formation is low at 420°C and 30 min (2.1%) but increases at this temperature with contact time reaching 7.4% at 60 min. This coke is essentially derived from maltene-polyaromatics and asphaltenes.

From the previous experiments it was realized that the interplay between maltenes-polyaromatics and asphaltenes and at a lesser extent the polar aromatics was the determining factor in the uncatalyzed hydrocracking reactions. Thus a new series of experiments were conducted in the microautoclave using the maltenes only. The results clearly indicate that the polyaromatics and polar compounds convert into asphaltenes which in turn form coke. This tendency goes in parallel with the rupture of alkyl chains which convert to saturates. These processes begin rather quickly for the maltenes derived from the particular vacuum bottoms treated. In fact, at 400°C and 60 min the breakdown of the polyaromatics (63.6% in the initial maltenes and 45.3% in the treated material) and of polars (25.6% and 16.8% respectively) results in the formation of saturates (5.6% to 17.4%) and gas (3.4%) as well as asphaltenes (8.3%) and some coke (0.7%). With increasing severity, the decrease in polyaromatics and polars is quite marked (down to 16.5% and 3.2% of total treated material at 460°C and 30 min) but the formation of asphaltenes (14.8%) and coke (13.0%) is also significant. It was also found that the formation of coke could be minimized while maintaining high conversions of polyaromatics and polars. Thus, at 440°C and 30 min the polyaromatics have decreased down to 21.8% and the polars to 4% while the saturates reach 30.6% and the asphaltenes 15.0%. The coke is maintained at 1.2% and the gas formation at 8.6%. These experiments proved the central role that polyaromatics and polars play in during hydrocracking.

A restricted number of experiments were conducted under catalytic hydrocracking. Iron sulfide, prepared at CANMET, was used as catalyst at concentrations of 5% and 15% weight of catalyst (per 100 weight of feedstock). Both the vaccuum bottoms and their derived maltenes were treated at 445°C for 30 min. These catalytic tests reduced the amount of coke formed, with respect to the non-catalytic hydrocracking in both the vacuum bottoms and the maltenes. They did not lower the asphaltene formation and they decrease the formation of saturates while increasing the polars when compared with the results of the non-catalytic experiments. More work is needed in this direction to ascertain the trends so far shown.

The asphaltenes derived from the bitumen vacuum topped bottoms were treated under non-catalytic hydrocracking conditions at 445-450°C for 15 min. Since the asphaltenes are solids, slurrying them with a solvent is a treatment which mimics their behaviour during hydrocracking. Tetralin (an interactive H-donor solvent) and decalin (a non-interactive solvent) were used at ratios slightly above 2:1 (solvent: asphaltene). It was clearly demonstrated that the presence of tetralin lowers the coke formation. Thus, starting from 100% asphaltenes, the treated material contains 2.5% coke, 8.5% asphaltenes and 78.5% maltenes when hydrocracking was conducted in the presence of tetralin and 12.3% coke, 17.8% asphaltenes and 65.6% maltenes in the presence of decalin. The comparative experiment with the heavy oil (having 38.8% asphaltenes) gave 8.4% coke, 17.9% asphaltenes and 70.3% maltenes. It was thus clear that the maltenes act as hydrogen donors during hydrocracking. Further studies along these lines are needed to understand which fraction of the maltenes act as a H-donor during hydrocracking.

As a conclusion to this phase of the project, we wish to emphasize that the approach of monitoring the distinct maltene fractions during hydrocracking leads to new insights into the interplay of these fractions. Although more work is needed along the lines indicated, it is clear that the decisive aspects of the hydrocracking reactions are the interconversions polyaromatics - polars - asphaltenes with coke being a later consequence of specific condensations. If we monitor the fractions of the asphaltenes as we have done with the maltenes, a more precise understanding of these interconversions will be gained. This is the objective of the second phase of this project now underway.

In summary, the approach shown in this work allows to develop a much better picture of the hydrocracking process. It can be used as a monitoring tool to optimize operational conditions and through processing of the individual fractions particularly maltenes-polyaromatics and maltenes-polars it is expected that clear and precise guidelines can be obtained on yields and product distribution from catalytic and non-catalytic hydrocracking.